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ANALYSIS OF NATURAL GAS AND ILLUMINATING GAS BY FRACTIONAL DISTILLATION AT LOW TEMPERATURES AND PRESSURES

BY

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By G. A. Burrell, F. M. Seibert, and I. W. Robertson.

INTRODUCTION.

This publication, which is one of a series dealing with the increase of efficiency in the production and utilization of fuels, describes in detail the results of experiments, made by the Bureau of Mines, with a method of separating and determining the hydrocarbons in gaseous fuels. The method employs fractional distillation in a vacuum at low temperatures. The gas is liquefied, the different constituents separated by proper adjustment of temperatures, the various fractions removed with a mercury pump, and these fractions analyzed by ordinary slow-combustion methods. The method was successfully applied to the separation of hydrocarbons in natural gas and in artificial illuminating gas, and is the only known method applicable to the separation of some hydrocarbons.

The first part of this report describes the results of experiments by which the natural gas used in Pittsburgh, Pa., was separated into its individual paraffin hydrocarbons. The second part describes experiments in which the separation of the illuminants in artificial illuminating gas, that used in Pittsburgh, Pa., and that used in New York City, was effected. Some experiments to determine the practicability of separating gases whose boiling points lie close together, such as ethane and ethylene, are included.

Each year much experimental work is done in the destructive distillation of different fuels, liquid, gaseous, and solid, which yield complex mixtures of different hydrocarbon gases. In reports on these tests some of the gases are not separated, but are invariably lumped together as illuminants (determined by absorption in fuming sulphuric acid, or bromine water) or calculated in the combustion analysis as methane and ethane. By the methods described in this publication the gases can be separated into the individual constituents. Hence a wide field of investigation is opened up, in that a much more exact study of combustion processes can be made and chemical changes more closely followed and better understood.

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PREVIOUS WORK ON THE FRACTIONAL DISTILLATION OF GASES.

The most notable work on the separation of gases by fractional distillation is that of Ramsey on the gases of the atmosphere. A detailed account of these experiments is given by Travers,[a] one of Ramsey's coworkers.

To start the experiments, 15 liters of argon and other rare gases were prepared from atmospheric air by absorbing the nitrogen with magnesium and the oxygen with metallic copper. After the argon and other constitutents had been liquefied by means of liquid air boiling under reduced pressure, the lower-boiling constituents of the liquefied argon, etc., were drawn off as a fraction rich in neon and containing helium. By many fractionations there was finally obtained a fraction that was almost pure neon. The separation of neon from helium and argon was finally accomplished by cooling the two gases with liquid hydrogen.

The first fraction contained much helium, the second fraction was collected separately, and the third fraction was collected after the removal of the liquid hydrogen. The second fraction, which should consist of neon chiefly, was then recondensed, and a small quantity of it evaporated back into the pump. The remainder of this second fraction was considered to be pure neon, the last traces having been discarded as probably containing traces of argon.

For the separation of krypton and zenon a much larger quantity of the inactive gases of the atmosphere was taken than in the case of neon and helium. After about 40 fractionations krypton and zenon were obtained in what was considered a pure condition.

Travis makes reference to the liquefaction of other gases; for instance, to the separation of ethylene from carbon monoxide.[b] In this case the mixed gases are slowly passed through a glass vessel surrounded with liquid air. At this temperature ethylene solidifies, and the rate of flow is made slow enough, so that practically the whole of the ethylene condenses while the carbon monoxide passes on through to a collecting chamber. To obtain pure ethylene the carbon monoxide, contaminated perhaps with traces of ethylene, can be again returned through the vessel which is surrounded by liquid air.

Although Ramsey and Travers showed that gas mixtures could be studied by fractionation, their work was confined chiefly to the rare gases of the atmosphere and to the preparation of pure gases.

In 1910 Stoltzenberg[c] and Erdman and Stoltzenberg[d] constructed an apparatus after the principle of the one described by Travers. Different gas mixtures, for instance ethylene and hydrogen, ethylene and oxygen, carbon dioxide and oxygen, and nitrogen peroxide and oxygen, were passed through baths maintained at such a temperature that one of the constituents condensed while the other was collected in a burette provided to receive it. Nothing novel, however, was offered over the scheme proposed by Ramsey, except the application of the method to other mixtures than those mentioned by him. An apparatus of different construction is also shown.

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[a] Travers, M. W., The experimental study of gases, 1901, pp. 212–223.

[b] Travers, M. W., Op. cit., p. 211.

[c] Stoltzenberg, H., Apparat zur Gasanalyse durch Kondensation: Ber. Deut. chem. Gesell., Jahrg. 43, Bd. 2, 1910, p. 1708.

[d] Erdman, E., and Stoltzenberg, H., Gasanalyse durch Kondensation: Ber. Deut. Chem. Gesell., Jahrg. 43, Bd. 2, 1910, p. 1702.

Later Lebeau and Damiens[a] worked on the problem of separating gases by fractional distillation. Their method is similar to that used by Ramsey and Travers in separating argon, neon, and helium, namely, maintaining the gas mixture at a temperature that renders the vapor pressures of one or more constituents inappreciable and withdrawing those constituents that have appreciable vapor pressures.

Lebeau and Damiens separated the different gases they used in pairs and made no mention of the need of refractionating the first fractions in order to obtain pure constituents, but credit is due them for being the first to denote the temperatures at which pairs of the paraffin and olefine hydrocarbons can be separated.

The credit for fractionating gases so as to obtain single constituents in the pure condition must go back to the work of Ramsey and Travers. The authors of this paper followed essentially the same scheme as that used by Ramsey and Travers in separating neon from helium, although different temperatures and in some cases different methods of manipulation were necessary.

PREPARATION OF PURE GASES.

Gases may be prepared in a pure state by repeated fractionation. For instance, ethylene prepared by the action of sulphuric acid on ethyl alcohol may be freed from hydrogen and carbon monoxide and air (if the air has leaked into the generator or connections) by withdrawing with a vacuum pump the three latter gases from the mixture at the temperature of liquid air. Water vapor and alcohol vapor may be frozen out at a temperature of about −78° C., a convenient temperature to obtain. Carbon dioxide is best removed by first washing it out with caustic-potash solution.

This method of preparing pure gases has many advantages over other methods where impurities are washed out of impure gases by means of absorbents. The authors have purified methane, ethane, ethylene, propane, butane, butylene, carbon dioxide, and acetylene by the process. In fact, there are scarcely any gases that can not by carefully adjusting and using the proper temperature be purified so that they are pure enough for the finest density or vapor-pressure work.

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[a] Lebeau, P., and Damiens, A., Sur une méthode d'analyse des mélanges complexes d'hydrogène et d'hydrocarbures saturés gazeux: Compt. rend., t. 156, 1913, p. 325.

SEPARATION OF THE CONSTITUENTS OF NATURAL GAS.

In the following pages are described some experiments that resulted in the separation of samples of natural gas into the individual paraffin hydrocarbons present.

Natural gas may contain only methane as the combustible constituent or it may be a mixture containing large proportions of the higher gaseous paraffins. In some samples the latter predominate. In addition, there may be vapors of the liquid paraffin hydrocarbons present, and in some fields the proportion of these vapors may be large enough to warrant the building of a plant for the extraction of gasoline.

The natural gas used in Pittsburgh is a complex mixture and is typical of gas that is supplied to many cities to the extent of billions of cubic feet each year. The exact composition of this gas is of importance to the Bureau of Mines because of its use in the bureau's scientific investigations, such as the testing of explosives, safety lamps, electrical mining machinery, and other mining appliances. By the analytical method described herein it is possible to determine more exactly the quantity of the vapors of the liquid paraffins in a natural-gas mixture than has been possible heretofore. At many plants gas that contains enough of these vapors is compressed and cooled and the condensate is sold as gasoline.

It is generally known that ordinary gas analyses by combustion give little indication regarding the individual hydrocarbons present in a natural-gas mixture. Only the two predominating paraffins are shown.

NATURE OF EXPERIMENTS.

In the experiments reported in this paper natural gas was first liquefied by means of liquid air, and the different paraffin hydrocarbons were separated by properly adjusting temperatures and removing the various fractions with a mercury pump. The fractions were analyzed by the ordinary slow-combustion method. A separation of the gaseous paraffin hydrocarbons is possible because in the liquid condition the boiling points, at 760 mm., of the gaseous paraffins are rather widely separated. These boiling points are as follows: Methane, −160° C.; ethane, −93° C.; propane, −45° C.; N–butane, +1°C., and isobutane, −10° C. The two butanes were not separated. In order to obtain fractions large enough for accurate analyses the experiment given herein was started with about 1½ liters (1,531 c. c.) of gas. Other experiments were performed with various samples of natural gas in which smaller quantities were used. The sample of Pittsburgh natural gas as analyzed by the ordinary slow-combustion method contained the following constituents:

	Per cent.
Methane	79.2
Ethane	19.6
Nitrogen	1.2
Total	100.0

There is also about 0.03 per cent of carbon dioxide in the gas mixture. Carbon monoxide, hydrogen, and olefin hydrocarbons are not present.

PROCEDURE IN EXPERIMENTS.

The general arrangement of the apparatus used in the analyses is shown in figure 1. A Töpler pump is shown on the left of the figure. In the figure *a* represents a Dewar flask to hold the refrigerant used in cooling the gases; *b* is the glass liquifying bulb in which the gases are cooled; these are the essential parts of the apparatus; *d* is a gas analysis burette and *c* another gas container for measuring the gases prior to cooling (many of the different types of gas measuring burettes on the market may be used for measuring the gases), *e* is a mercury manometer for registering pressures in the Töpler pump; *f* is a drying tube containing phosphorus pentoxide for removing the water vapor from the gases; *g* and *h* are containers for trapping the gases over mercury as they are removed from the pump; container *h* is provided with a three-way stopcock. The particular advantage of a container such as is shown at *h* lies in the fact that while the stopcock is open to the air, it can be filled with mercury by forcing it down into the mercury which finally fills the capillary tubes on the stopcock. The gas from the pump can then be introduced into the container by means of the gooseneck tube attached to the tube *l*, so that a mercury seal is left in the capillary tube all the time. At *j* is shown a pressure gage, which was of use in the determination of benzene in illuminating gas, described in the second part of this report. At *o*, *n*, and *m* are three-way stopcocks. A counterpoise, *p*, attached to the mercury reservoir *i* of the Töpler pump greatly facilitated the working of the pump.

The gas sample prior to liquefaction was measured in the glass vessel *c*, then transferred to the gas burette *d*, and from there passed into the liquefying bulb *b*.

SEPARATION OF METHANE.

The entire sample was first completely liquefied at the temperature of liquid air. Connection was made between the container of the liquefied gas and the mercury pump, and as much as possible of the gas was removed by means of the pump. This process divided the original quantity into two parts—a gaseous part and a liquid residue.

That is, the vapor pressure of liquid ethane (normal boiling point −93° C.) is so small at the temperature of liquid air that no ethane

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could be detected in the distillate within the error allowable in making the analysis. The same is true of propane and butane. If use was made of liquid air that had stood for some time so that its boiling point had risen to a point near to the boiling point of oxygen (−183° C.), the methane and nitrogen were removed from the original mixture more quickly than when newly made liquid air was used. Such a result was to be expected. The residue from the first fractionation was allowed to volatilize, was then measured, and was again liquefied at the temperature of liquid air. Connection was

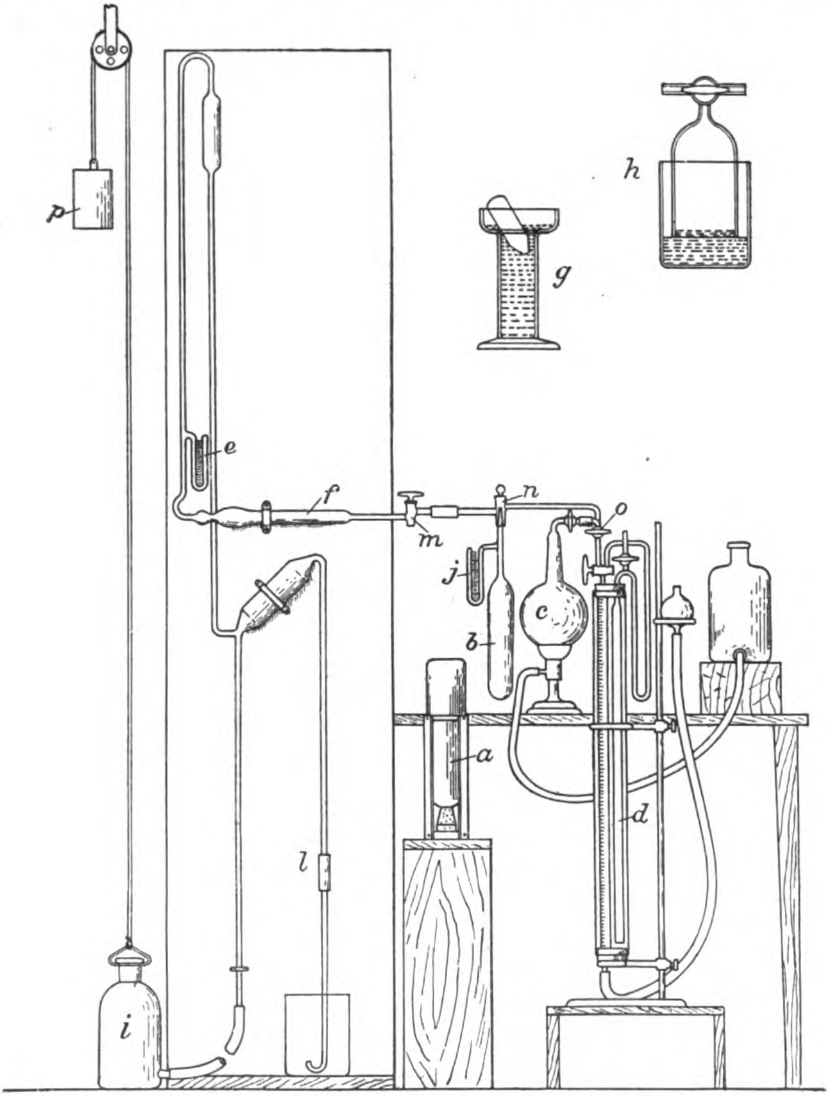

FIGURE 1.—Apparatus for liquefaction and fractionation of gases.

again made to the pump and more methane removed. Thus, although the residue from the first fractionation was treated in exactly the same manner as was the original sample, more methane was obtained. However, when the entire residue had been volatilized and again liquefied, the last methane part was obtained. In no test were the last traces recovered. Attempts at complete recovery were abandoned when it was found that a proportion was being left so small as not sensibly to affect the results.

At this point the first fractionation had removed the larger part of the methane, and the first residue had been volatilized, reliquefied, and the pump connected to obtain another small portion of methane. The residue from the second liquefaction was treated again in the same manner and more methane was obtained. A further identical treatment resulted in no additional recovery of methane. No indication of methane, within the error allowable in making the analysis, was found in the part that contained the ethane, propane, and higher paraffins.

The distillate obtained by the above procedure undoubtedly contained a trace of ethane, but the quantity was so small that it could not be detected by analysis. The results of analysis of a part of the total methane and nitrogen fraction follow:

Results of analyses of a part of a total methane and nitrogen fraction.

Item.	Analysis 1.	Analysis 2.
	C. c.	*C. c.*
Volume of sample taken	30.10	30.20
Volume of oxygen added	95.20	99.30
Total volume for combustion	125.30	129.50
Volume after combustion	66.30	70.10
Contraction from combustion	59.00	59.40
Volume after carbon dioxide absorption	36.80	40.50
Carbon dioxide from combustion	29.50	29.60
Methane from contraction[a]	29.44	29.64
Methane from carbon dioxide absorption[a]	29.59	29.67
	Per cent.	*Per cent.*
Methane from contraction	97.8	98.2
Methane from carbon dioxide absorption	98.3	98.2
Average methane	98.1	98.2

[a] Corrected for the molecular volume of CO_2.

SEPARATION OF ETHANE.

The next step in the process involved the separation of the ethane from the methane-free residue. In this step it was necessary to employ a temperature at which practically all of the ethane could be separated from the still higher paraffins, such as propane and the butanes. The temperature used could not have been too low, else the ethane itself could not have been removed; neither could the temperature have been so high as to cause all the propane to be removed. A natural-gas condensate, obtained from a plant for making gasoline from natural gas by subjecting natural gas (casing-head gas) from an oil well to a pressure of 250 pounds per square inch and then cooling it to ordinary temperatures, proved excellent, when cooled by liquid air, for obtaining temperatures higher than the temperature of liquid air. This condensate is known in the trade as "wild" gasoline. It contains large quantities of liquid propane and of butane (especially the latter), as well as some of the constituents of ordinary gasoline, such as pentane and hexane. Other substances that were tried for obtaining low temperatures, such as alcohol, ether, methyl, and ethyl chloride, jellied so much at low temperatures that they could not be used satisfactorily. The mass did not remain of uniform temperature from top to bottom, and stiffened so much at low temperatures that it could not be stirred.

In order to obtain a temperature of −140° C., for instance, the condensate was placed in a Dewar flask and stirred with a test tube, in which liquid air was run, until the condensate had reached the desired temperature. Upon removal of the test tube the condensate warmed up slowly, about 5° to 10° C. per hour, thereby affording sufficient time for withdrawing from the gas samples in the liquefaction bulb the particular vapors that were sought. In separating ethane from the methane-free residue, this residue was first cooled to a temperature of −140° C., then pumping was started and continued until the temperature had risen to −125° C. By this process there was obtained a distillate consisting of ethane and propane. In other words, some propane (boiling point −45° C.) was removed at −125° C., as well as the ethane (boiling point −93° C.). Residues and distillates were again treated, the final separation of the ethane being made at a temperature of −155° to −140° C. The temperature was purposely raised to −125° C., the first time in order that practically all of the ethane as well as some propane might be obtained, because it was found easier to separate the ethane from that part of the propane that came over than to attempt to remove all of the ethane from the original residue. All the ethane was obtained, only a small quantity of propane being left as a residue. The results of analyses of a part of the total ethane fraction follow:

Results of analyses of a part of a total ethane fraction.

Item.	Analysis 1.	Analysis 2.
	C. c.	*C. c.*
Volume of sample taken	25.50	20.30
Volume of oxygen added	96.60	99.40
Total volume for combustion	122.10	119.70
Volume after combustion	58.30	69.20
Contraction from combustion	63.80	50.50
Volume after carbon dioxide absorption	7.20	28.70
Carbon dioxide from combustion	51.10	40.50

According to the equation $C_2H_6+3.5O_2=2CO_2+3H_2O$, the contraction should be equal to the CO_2 multiplied by 1.25. In analysis 1 the contraction corresponding to the CO_2 content was 51.1 c. c., which, multiplied by 1.25, equals 63.87 c. c. This figure corresponds well with the contraction actually observed, which was 63.80 c. c. In analysis 2 the contraction corresponding to the CO_2 content was 40.50 c. c., which, multiplied by 1.25, equals 50.62. The contraction actually observed was 50.50 c. c. In calculating the ethane content from the carbon dioxide content and the contraction, use was made of equations that correct for the deviations of carbon dioxide and ethane contents from the ideal conditions,[a] the calculations being as follows:

Calculation for Ethane for Analysis 1.

$0.990C_2H_6+3.5O_2=1.992CO_2+3H_2O$.

Volume of ethane $=0.396\times$contraction$=0.396\times63.80=25.26$.

Volume of ethane $=0.497\times CO_2=0.497\times51.10=25.39$ c. c.

Calulation for Ethane for Analysis 2.

$0.990C_2H_6+3.5O_2=1.994CO_2+3H_2O$.

Volume of ethane $=0.397\times$contraction$=0.397\times50.50=20.05$.

Volume of ethane $=0.496\times CO_2=0.496\times40.50=20.09$ c. c.

SEPARATION OF PROPANE AND HIGHER PARAFFINS.

As indicated above, the final residue from the second series of fractionations contained propane and higher paraffins.

The methane and ethane free residue was liquefied and the gas pumped off at an initial temperature of −125° and a final one of −110° C., the object being to remove practically all of the propane (boiling point −45°) and also some of the butanes (boiling points +1° C. and −10° C.). The residue from this operation was again treated in the same manner to obtain any propane that still remained behind. It was found that if a temperature was used that would permit the distillation of an appreciable quantity of butane, practically all of the propane would come over. The total distillate obtained in this manner was then liquefied and the gas pumped off at a temperature ranging from −135° to −120° C. There resulted a distillate that consisted of propane only. In other words, propane can be separated from the butane at a temperature of −135° to −120° C.

The results of analyses of parts of the total propane fraction follow:

Results of analyses of a part of a total propane fraction.

Item.	Analysis 1.	Analysis 2.
	C. c.	*C. c.*
Volume of sample taken	12.60	13.30
Volume of oxygen added	93.80	97.20
Total volume for combustion	106.40	110.50
Volume after combustion	67.60	70.00
Contraction from combustion	38.80	40.50
Volume after carbon dioxide absorption	28.50	29.70
Carbon dioxide from combustion	39.10	40.30

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[a] See Burrell, G. A., and Seibert, F. M., Errors in gas analysis due to assuming that the molecular volumes of all gases are alike: Technical Paper 54, Bureau of Mines, 1913, p. 11.

According to the equation $C_3H_8 + 5O_2 = 3CO_2 + 4H_2O$, the contraction minus the CO_2 equals 0.0. In analysis 1, 38.8 c. c. − 39.1 c. c. = − 0.3 c. c., and in analysis 2, 40.5 c. c. − 40.3 c. c. = 0.2 c. c. The propane content was calculated from the following corrected equation:

$$0.986C_3H_8 + 5O_2 = 2.991CO_2 + 4H_2O.$$

Then according to analysis 1 the propane content when calculated from the contraction is 0.329 × 38.80 = 12.76 c. c., and when calculated from the CO_2 absorption is 0.329 × 39.10 = 12.86 c. c.

According to analysis 2 the propane when calculated from the contraction is 0.329 × 40.5 = 13.32 c.c., and when calculated from the CO_2 absorption is 0.329 × 40.3 = 13.26 c. c.

In the case of both analyses the volume of propane as calculated from the CO_2 absorption and the contraction agree closely.

The value 0.986, or the molecular volume of propane at 0° C. and 760 mm. of mercury was calculated from Van der Waals's equation, in which the ratio between the pressure P, the volume V, and the temperature T of a gas is expressed thus:

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT$$

Further, if d = density at 0° C. and 760 mm. pressure and M the molecular weight, the following equation is derived:

$$\frac{M}{d_0}(1+a)\ (1-b)=R$$

Lebeau [a] gives for a the value 0.01727 and for b the value 0.003770, from which $\frac{M}{d}=\frac{22.412}{1.0133}=22.116$, and $\frac{22.116}{22.412}=0.986$.

This value, so far as the authors are aware, has never been determined experimentally as have the molecular volumes of oxygen, methane, ethane, and carbon dioxide.

The same procedure was followed for the propane separation as for the ethane and the methane separations. Distillates and residues were liquefied and the gases pumped off until no appreciable quantity of propane could be obtained.

The results of analysis of a part of the final residue follow. The residue should consist of butane only, provided no vapors of the liquid paraffins were present.

Results of analysis of a part of a total butane fraction.

Item.	C.c.
Volume of sample taken	9.30
Volume of oxygen added	100.00
Total volume for combustion	109.30
Volume after combustion	76.30
Contraction from combustion	33.00
Volume after carbon dioxide absorption	39.30
Carbon dioxide from combustion	37.00

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[a] Landolt and Börstein, Physikalisch-chemische Tabellen, 1912, p. 445 (by Lebeau).

According to the equation $C_4H_{10}+5O_2=4CO_2+5H_2O$, the contraction multiplied by 1.14 equals the CO_2 content. The contraction of 33.0 c. c., shown by the above analysis, multiplied by 1.14 equals 37.62 c. c., which, less 37.00 c. c., equals 0.62 c. c. difference.

The above analysis was calculated to butane only, and the fraction appears to have been almost entirely that gas, but undoubtedly a small proportion of the vapors of the liquid paraffins were contained in the mixture.

INDICATIONS AFFORDED BY VAPOR PRESSURES.

Vapor pressures obtained by means of a manometer attached to the pump furnished evidence as to when a separation had been accomplished. For instance, at the temperature of liquid air that has stood exposed to the air for some time the vapor pressure of the hydrocarbon mixture was 63 mm. Approximately that pressure persisted throughout the pumping until near the end, when it suddenly dropped to 0.0 mm. Then the pumping was stopped and the residue allowed to volatilize, when it was again liquefied and the pumping continued until no more distillate was obtained. Three liquefactions of the residues were usually necessary to remove all the methane.

When the methane-free and nitrogen-free residue was liquefied for the removal of the ethane, the vapor pressure of the mixture was about 2 mm. at −155° C. and about 4 mm. at −145° C. When nearly all the ethane had been removed, the pressure dropped suddenly to 0.0 mm. The residue was then again liquefied and treated in the same manner until all the ethane had been removed. Three successive treatments of the residue were usually sufficient.

After the removal of the nitrogen, methane, and ethane from the mixture had been accomplished it became necessary to separate the propane from the butane, etc. The separation was finally made at −130° to −120° C. The vapor pressure at −130° C. was about 0.5 mm. and about 1 mm. at −125° C. The pressure dropped suddenly to 0.0 mm. after nearly all the propane had been removed. The residues were then treated as previously described until all the propane had been removed. The final residue consisted of the butane and any vapors of the liquid hydrocarbons that were present.

The various steps in the separation of the natural gas into its constituents by means of fractional distillation at low temperatures are shown in figure 2. The original volume of the sample was 1,531.0 c. c. The sample was first liquefied at the temperature of liquid air, and a distillate of 1,311.3 c. c. was obtained with the mercury pump; a residue of 219.7 c. c. was left behind. Both the residue and the distillate were again treated at the temperature of liquid air. From

Constituent.	Cubic centimeters.	Per cent.
Nitrogen...	23.8	1.6
Methane...	1,297.4	84.7
Ethane....	144.5	9.4
Propane...	46.1	3.0
Butane (chiefly).	19.2	1.3
Total....	1,531.0	100.0

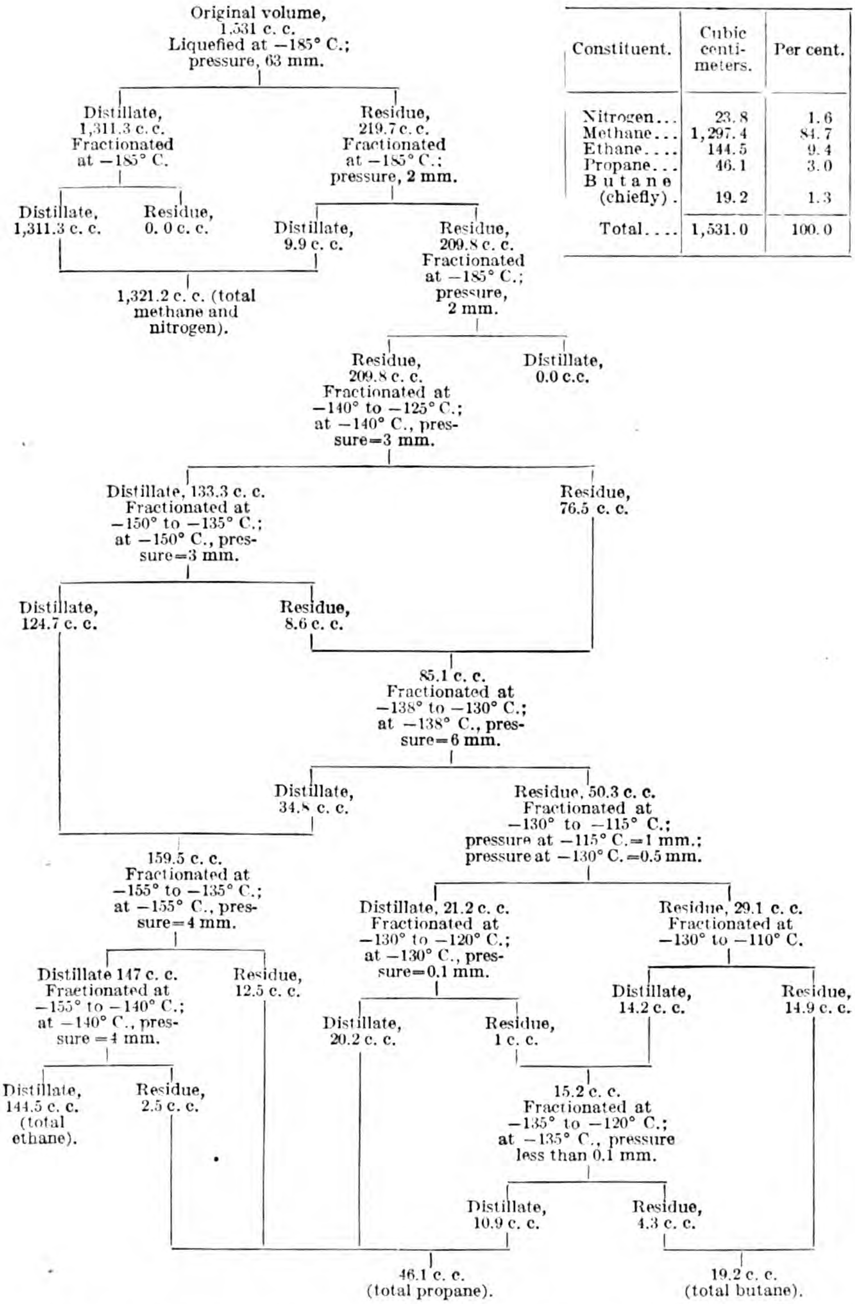
Original volume, 1,531 c. c. Liquefied at −185° C.; pressure, 63 mm.
Distillate, 1,311.3 c. c. Fractionated at −185° C.
Residue, 219.7 c. c. Fractionated at −185° C.; pressure, 2 mm.
Distillate, 1,311.3 c. c.
Residue, 0. 0 c. c.
Distillate, 9.9 c. c.
Residue, 209.8 c. c. Fractionated at −185° C.; pressure, 2 mm.
1,321.2 c. c. (total methane and nitrogen).
Residue, 209.8 c. c. Fractionated at −140° to −125° C.; at −140° C., pressure=3 mm.
Distillate, 0.0 c.c.
Distillate, 133.3 c. c. Fractionated at −150° to −135° C.; at −150° C., pressure=3 mm.
Residue, 76.5 c. c.
Distillate, 124.7 c. c.
Residue, 8.6 c. c.
85.1 c. c. Fractionated at −138° to −130° C.; at −138° C., pressure=6 mm.
Distillate, 34.8 c. c.
Residue, 50.3 c. c. Fractionated at −130° to −115° C.; pressure at −115° C.=1 mm.; pressure at −130° C.=0.5 mm.
159.5 c. c. Fractionated at −155° to −135° C.; at −155° C., pressure=4 mm.
Distillate, 21.2 c. c. Fractionated at −130° to −120° C.; at −130° C., pressure=0.1 mm.
Residue, 29.1 c. c. Fractionated at −130° to −110° C.
Distillate 147 c. c. Fractionated at −155° to −140° C.; at −140° C., pressure = 4 mm.
Residue, 12.5 c. c.
Distillate, 14.2 c. c.
Residue, 14.9 c. c.
Distillate, 20.2 c. c.
Residue, 1 c. c.
Distillate, 144.5 c. c. (total ethane).
Residue, 2.5 c. c.
15.2 c. c. Fractionated at −135° to −120° C.; at −135° C., pressure less than 0.1 mm.
Distillate, 10.9 c. c.
Residue, 4.3 c. c.
46.1 c. c. (total propane).
19.2 c. c. (total butane).

FIGURE 2.—Diagram showing various steps in the separation of the constituents of natural gas by means of fractional distillation at low temperatures.

the residue was obtained 9.9 c. c. more of methane, but no residue remained behind upon treating the distillate of 1,311.3 c. c. The sum of 9.9 c. c. and 1,311.3 c. c. represented practically all of the methane and the nitrogen in the natural-gas sample. The distillate from the reliquefaction of the residue contained no methane, as shown by a further treatment at the temperature of liquid air.

After the methane had been separated there remained a residue, which, on evaporation, gave a volume of 209.8 c. c., and consisted of ethane and higher paraffin hydrocarbons. The residue was liquefied at temperatures ranging from −140° to −125° C., and as much gas as possible was removed with the pump. Ethane and some propane (133.3 c. c.) were obtained; a residue of 76.5 c. c. remained. The distillate was then cooled to temperatures ranging from −150° to −135° C.; a distillate of 124.7 c. c. and a residue of 8.6 c. c. were obtained. The 8.6 c. c. residue was added to the 76.5 c. c. residue and the total, 85.1 c. c., cooled to −138° to −130° C. and pumped. The distillate of 34.8 c. c. was added to the 124.7 c. c. distillate previously obtained, and the total was cooled at a temperature that did not rise above −135° C. There was obtained a distillate of 147.0 c. c. and a residue of 12.5 c. c. The 147 c. c. of distillate was then cooled and the gas removed while the temperature of the distillate was not higher than −140° C. The distillate (144.5 c. c.) was pure ethane. The residue (2.5 c. c.) from the last treatment was added to the rest of the methane-free and ethane-free gas for the propane treatment. The separation of the propane and the butane was carried on in a manner similar to that in which the methane and ethane separations were performed, except that higher temperatures were used.

DETERMINATION OF THE PARAFFIN HYDROCARBONS IN A SO-CALLED "WET" GAS.

In separating the paraffin hydrocarbons in a natural gas from which gasoline is extracted at a plant in West Virginia, the authors used a procedure essentially the same as that described above for the fractionation of the natural gas of Pittsburgh. The marked differences in the proportions of the different hydrocarbons present is of interest.

FIRST SERIES OF FRACTIONATIONS.

Figure 3 shows the various steps in the work. The original volume of the sample was 185.3 c. c. At a temperature of −193° C. 78.5 c. c. of gas was withdrawn; the residue, on evaporation, gave 106.8 c. c. of gas. Both the residue and the distillate were reliquefied at the temperature of liquid air, to obtain, as shown by analyses, pure methane, mixed with air and nitrogen. This distillate amounted to 83.5 c. c. Air was originally present in the sample owing to leaks in the gas pipes at the gasoline plant. The gas was drawn from the wells under a pressure of about 500 m. m. of mercury. The final analysis was calculated air free as given on page 19 to show the constituents originally present in the gas.

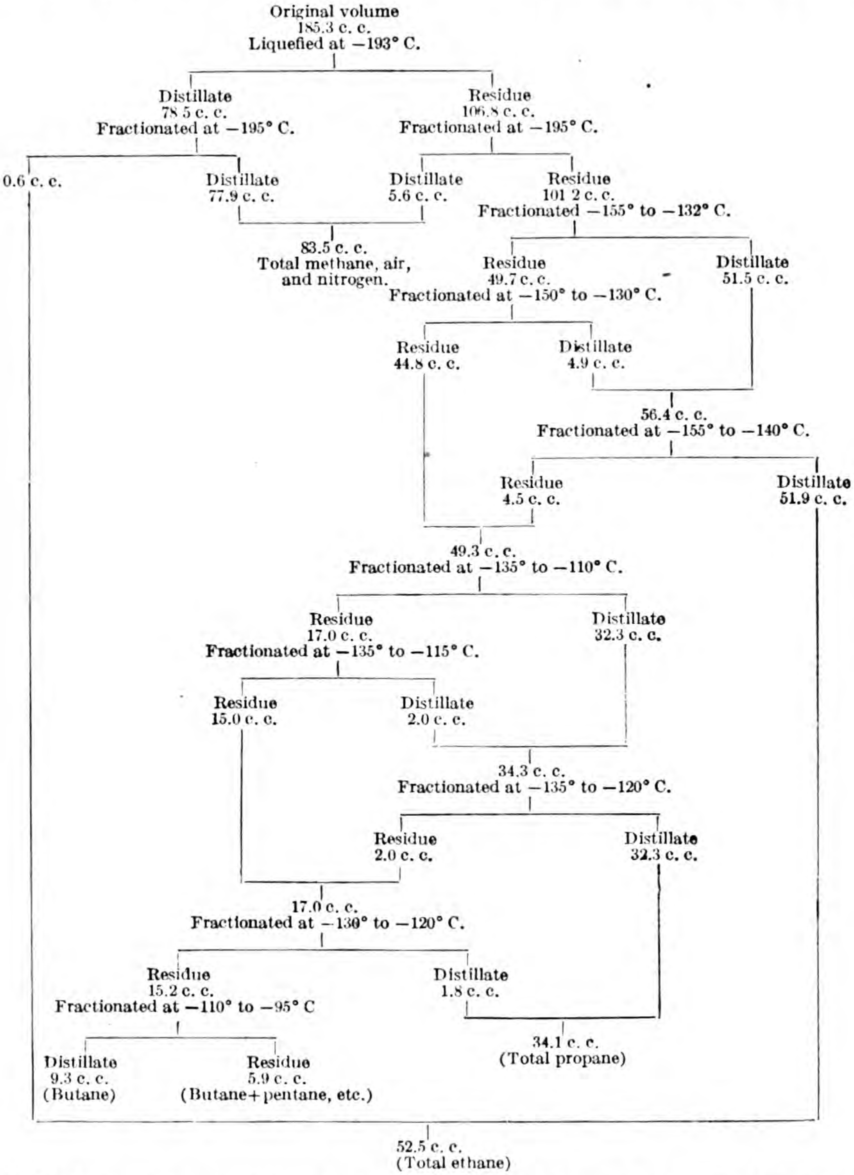

FIGURE 3.—Diagram showing various steps in the separation of the paraffin hydrocarbons present in a natural gas from which gasoline is extracted.

SECOND SERIES OF FRACTIONATIONS.

After the removal of the methane the residue, 101.2 c. c., contained ethane and higher paraffin hydrocarbons. The residue was liquefied and distilled, and the resulting distillate and residue liquefied and distilled until finally, at a temperature that ranged from −155° to −140° C., the distillate obtained, 51.9 c. c., was pure ethane. To this was added 0.6 c. c. of ethane obtained in the first series of fractionations, when the methane was separated, making a total of 52.5 c. c. of ethane.

THIRD SERIES OF FRACTIONATIONS.

After the removal of the ethane the total residue amounted to 49.3 c. c. of propane and higher paraffin hydrocarbons. The final fractionation in this series was made at a temperature not higher than −120° C., and yielded 34.1 c. c. of pure propane. The fractionations were carried to a point where only a small quantity (1.8 c. c.) of propane was obtained.

FOURTH SERIES OF FRACTIONATIONS.

After the removal of the propane there remained a residue of 15.2 c. c. that contained butane and higher paraffin hydrocarbons.

A separation of this residue into two parts was made by removing some gas with the pump when the temperature was not higher than −95° C. An analysis of the distillate indicated that the chief constituent was butane. It is certain that some of the butane remained in the residue and that the distillate of 9.3 c. c. contained at least a small quantity of pentane; hence it is better to designate the 15.2-c. c. residue as butane and higher paraffin hydrocarbons.

Air is not found in natural gas as it occurs in the wells, and should be eliminated from consideration. There is, however, about 1 per cent of nitrogen present and about 0.03 per cent of carbon dioxide, which are not shown in the results as presented.

Results of fractionation analyses of a "wet" natural gas.

Constituent.	Volume.	Proportion of constituent in sample as received.	Air-free proportion.
	C. c.	*Per cent.*	*Per cent.*
Air and nitrogen	24.5	13.2	....
Methane	59.0	31.9	36.8
Ethane	52.5	28.3	32.6
Propane	34.1	18.4	21.1
Butane and pentane	9.3 } 15.2	5.0 } 8.2	5.8 } 9.5
Hexane, etc	5.9	3.2	3.7
Total	185.3	100.0	100.0

The quantities of the several paraffins in this gas mixture differ from those in the one first described. The latter represented a gas used in certain States in immense quantities for domestic and other purposes; the other represented a casing-head natural gas used in the making of gasoline.

MEASUREMENT OF TEMPERATURES.

Temperature measurements, made with two pentane thermometers, agreed closely. The determined melting point of chloroform was $-62°$ C., and of carbon disulphide $-111°$ C., and gave $-193°$ C. for the boiling point of fresh liquid air. The true melting point of chloroform is $-63.7°$ C.,[a] and of carbon disulphide $-111.6°$ C.[a]

SEPARATION OF ILLUMINANTS IN ARTIFICIAL ILLUMINATING GAS.

NATURE OF EXPERIMENTS.

In experiments made by the authors on the separation of the illuminants in artificial illuminating gas, the Pittsburgh, Pa., gas was first tried. This gas is made by mixing 1 part of carburetted water gas with 3 parts of coal gas. Separation of the illuminants was effected by fractionally distilling the gas in a vacuum at low temperatures, after the method for separating the hydrocarbons of natural gas, as outlined in the first part of this report.

EXPERIMENTS WITH PITTSBURGH GAS.

At different stages in the analysis the gas was subjected to temperatures at which certain constituents could be removed by a mercury pump from certain others that have lower vapor pressures. Distillates and residues were refractionated until the separation was as nearly perfect as was desired.

BOILING POINTS OF CONSTITUENTS IN ARTIFICIAL GAS.

The different constituents of artificial gas are listed below in groups according to the different temperatures at which they can be separated. The distillates that can be obtained at a particular temperature are shown, as well as the residues; that is, those gases that have inappreciable vapor pressures at the temperature given.

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[a] Henning, F., The fixation of the temperature scale between 0°C. and $-193°$ C.: Ann. der Phys., vol. 43, 1913, p. 294.

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Constituents of artificial illuminating gas grouped according to temperatures at which they separate.

CONSTITUENTS THAT SEPARATE AT TEMPERATURES OF LIQUID AIR.

Distillate.	Boiling point.	Residue.	Boiling point.
	° C.		*° C.*
Methane (CH_4)	−160	Ethane (C_2H_6)	− 93
Nitrogen (N_2)	−195	Propane (C_3H_8)	− 45
Oxygen (O_2)	−183	N-butane (C_4H_{10})	1
Carbon monoxide (CO)	−190	Isobutane (C_4H_{10})	− 10
Hydrogen (H_2)	−253	Ethylene (C_2H_4)	−103
		Propylene (C_3H_6)	− 51
		Isobutylene (C_4H_8)[a]	− 4
		Benzene (C_6H_6)	80

−150° C. TO −140° C.

Ethylene (C_2H_4)	−103	Propane (C_3H_8)	−45
Ethane (C_2H_6)	− 93	N-butane (C_4H_{10})	1
		Isobutane (C_4H_{10})	−10
		Propylene (C_3H_6)	−51
		Isobutylene (C_3H_8)	− 4
		Benzene (C_6H_6)	80

−135° C. TO −120° C.

Propane (C_3H_8)	−45	N-butane (C_4H_{10})	1
Propylene (C_3H_6)	−51	Isobutane (C_4H_{10})	−10
		Isobutylene (C_4H_8)	− 4
		Benzene (C_6H_6)	80

−78° C.

N-butane (C_4H_{10})	1	Benzene (C_6H_6)	80
Isobutane (C_4H_{10})	−10		
Isobutylene (C_4H_8)	− 4		

[a] The boiling point of N-butylene could not be found in the literature. The N-butylene was not separated from the isobutylene nor was the N-butane separated from the isobutane.

COMPOSITION OF THE ARTIFICIAL GAS OF PITTSBURGH.

The artificial gas of the city of Pittsburgh, Pa., was analyzed by ordinary methods on September 1, 1914, with the following results:

Results of analysis of artificial gas of Pittsburgh, Pa.

Constituent.	Per cent.
Carbon dioxide (CO_2)	2. 64
Oxygen (O_2)	. 81
Illuminants	8. 67
Carbon monoxide (CO)	13. 34
Hydrogen (H_2)	37. 04
Methane (CH_4)	30. 96
Ethane (C_2H_6)	1. 82
Nitrogen (N_2)	4. 72
	100. 00

In making the analysis the carbon dioxide was removed by the caustic potash solution, the oxygen by alkaline pyrogallate solution, the illuminants by fuming sulphuric acid, the hydrogen by absorption in colloidal palladium solution, and the methane and ethane by slow combustion, and the nitrogen was determined by difference.

PROCEDURE IN EXPERIMENTS.

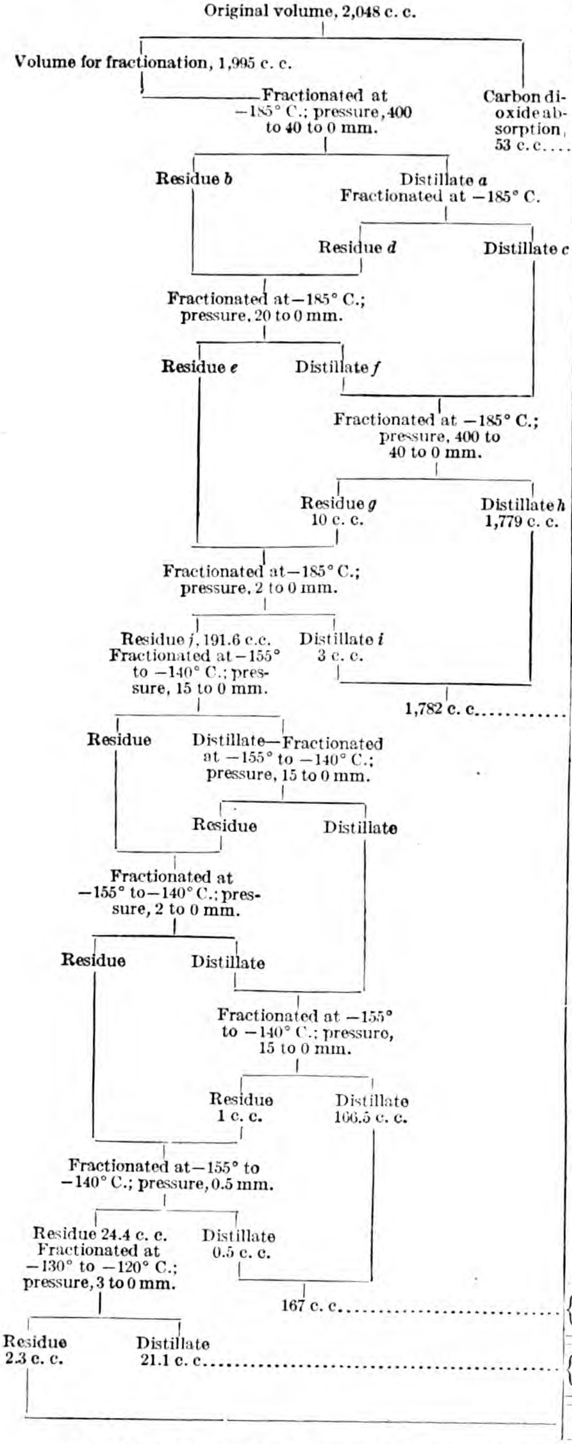
The gas was subjected to fractional distillation at various low temperatures in the apparatus shown in figure 1. A description of the apparatus and the method of using it will be found on pages 9 to 15.

FIRST SERIES OF FRACTIONATIONS.

Figure 4 shows the principal steps in the separation of the gas.

The original volume of gas taken for analysis was 2,048 c. c. This was first freed of the carbon dioxide by passing it through caustic potash solution; 53 c. c. of carbon dioxide was removed, leaving 1,995 c. c. The 1,995 c. c. of gas was then cooled in the bulb *b* (fig. 1), in portions of about 300 c. c. at a time, at the temperature of liquid air. After the introduction of each 300 c. c., pumping was started and as much of the gas removed as possible. There resulted a distillate, *a*, and a residue, *b*. The distillate *a* was fractionated at the temperature of liquid air, resulting in two more fractions, *c* and *d*. Fraction *d* was added to the residue *b*, and this part again fractionated at the temperature of liquid air. The distillate *f* thus obtained was added to the distillate *c*, and this part again fractionated at the temperature of liquid air. The residue *g* thus obtained (10 c. c.) was added to the residue *e* and this part again fractionated. There resulted a distillate, *i*, of 3 c. c. which was added to the distillate *h*, making a total of 1,782 c. c. This first series of fractionations shows the general procedure. At the temperature adopted, in this case the temperature of liquid air, the gases were repeatedly fractionated until no more distillate in sufficient quantity to be of consequence could be obtained. Three c. c., the quantity of final distillate obtained, is only about 0.15 per cent of 2,048 c. c., the original quantity of gas taken for the experiment.

The total distillate obtained at the temperature of liquid air, 1,782 c. c., consisted of those gases that have an appreciable vapor tension at that temperature. This fraction consisted of 0.81 per cent of oxygen, 13.25 per cent of carbon monoxide, 37.33 per cent of hydrogen, 31.13 per cent of methane, and 4.23 per cent of nitrogen. It will be observed that the quantities of these constituents check well with the quantities of the same constituents found in the original analysis of the coal gas by the ordinary method (p. 21). The residue *j* of the first series of fractionations (191.6 c. c.) should consist of those gases and vapors that do not have an appreciable vapor pressure at the


Original volume, 2,048 c. c.
Volume for fractionation, 1,995 c. c.
Fractionated at −185° C.; pressure, 400 to 40 to 0 mm.
Carbon dioxide absorption, 53 c. c.
Residue b
Distillate a Fractionated at −185° C.
Residue d
Distillate c
Fractionated at −185° C.; pressure, 20 to 0 mm.
Residue e
Distillate f
Fractionated at −185° C.; pressure, 400 to 40 to 0 mm.
Residue g 10 c. c.
Distillate h 1,779 c. c.
Fractionated at −185° C.; pressure, 2 to 0 mm.
Residue j, 191.6 c.c. Fractionated at −155° to −140° C.; pressure, 15 to 0 mm.
Distillate i 3 c. c.
1,782 c. c.
Residue
Distillate—Fractionated at −155° to −140° C.; pressure, 15 to 0 mm.
Residue
Distillate
Fractionated at −155° to −140° C.; pressure, 2 to 0 mm.
Residue
Distillate
Fractionated at −155° to −140° C.; pressure, 15 to 0 mm.
Residue 1 c. c.
Distillate 166.5 c. c.
Fractionated at −155° to −140° C.; pressure, 0.5 mm.
Residue 24.4 c. c. Fractionated at −130° to −120° C.; pressure, 3 to 0 mm.
Distillate 0.5 c. c.
167 c. c.
Residue 2.3 c. c.
Distillate 21.1 c. c.

COMPOSITION OF FRACTION.

Constituent.	C. c.	Proportion in sample, percent.
Carbon dioxide (CO_2)	53	2.63
Oxygen (O_2)	16.6	.81
Carbon monoxide (CO_2)	271.4	13.25
Hydrogen (H_2)	764.5	37.33
Methane (CH_4)	637.5	31.13
Nitrogen (N_2)	92.0	4.23
Ethylene (C_2H_4)	124.0	6.05
Ethane (C_2H_6)	43.0	2.10
Propylene (C_3H_6)	12.3	.60
Propane (C_3H_8)	8.8	.43
Butylene (C_4H_8)	2.3	0.11

FIGURE 4.—Diagram showing various steps in fractionation of artificial illuminating gas.

temperature of liquid air. They are C_2H_6, C_3H_8, C_4H_{10}. C_2H_4, C_3H_6, C_4H_8, and C_6H_6—in other words, the so-called illuminants of coal gas, with the addition of ethane and probably propane.

SECOND SERIES OF FRACTIONATIONS.

The residue *j* (191.6 c. c.) was next cooled at temperatures ranging from −155° C. to −140° C., and as much gas as possible removed with the mercury pump. Distillates and residues were repeatedly fractionated until there was obtained 167.0 c. c. of gas consisting of ethane and ethylene. This fraction was analyzed in two ways, (1) by burning some of it with oxygen, and (2) by first removing the ethylene with fuming sulphuric acid and then burning the ethane in oxygen. The data covering these two methods of analysis follow:

Results of analysis of ethane and ethylene.

ANALYSIS BY COMBUSTION.

Volume of sample taken	cubic centimeters	15.12
Volume of oxygen added	do	94.42
Total volume for combustion	do	109.54
Volume after combustion	do	78.00
Contraction from combustion	do	31.54
Volume after carbon dioxide absorption	do	48.27
Carbon dioxide from combustion	do	29.73
Ethane	per cent	23.90
Ethylene	do	74.40

ANALYSIS BY ABSORPTION AND COMBUSTION.

Volume of sample taken	cubic centimeters	34.18
Volume after absorption in fuming H_2SO_4	do	8.85
Volume absorbed by fuming H_2SO_4	do	25.33
Volume of oxygen added	do	76.28
Total volume for combustion	do	85.13
Volume after combustion	do	64.95
Contraction from combustion	do	20.18
Volume after carbon dioxide absorption	do	49.02
Carbon dioxide from combustion	do	15.93
Ethane	per cent	23.3
Ethylene	do	74.1

The percentages of ethane and of ethylene, as found by the two methods of analysis, check well, showing that other gases were not present in the distillate in significant amounts. The two percentages for each gas as found above were averaged and calculated to percentage of the original coal gas.

THIRD SERIES OF FRACTIONATIONS.

After the removal of the ethane and ethylene there remained 24.4 c. c. of gas, which was fractionated at temperatures ranging from −130° C. to −120° C. The distillate, 21.1 c. c., was analyzed by

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burning it in oxygen, measuring the resulting contraction and the carbon dioxide absorption and calculating the results to propane and propylene. This method does not isolate the gases and hence does not show that this distillate contained no gases other than propane and propylene. In the experiments on the separation of the paraffin hydrocarbons in natural gas, however, it was found that propane could be separated from ethane at temperatures between −130° C. and −120° C. The boiling point of propylene is very close to that of propane, and the boiling point of ethylene does not differ much from that of ethane, hence it was assumed that propylene and ethylene would respond to the same treatment as propane and ethane.

FOURTH SERIES OF FRACTIONATIONS.

After the propylene and propane had been removed there remained a residue of 2.3 c. c., only 0.11 per cent of the original quantity, 2048 c. c., of gas. This residue was burned in oxygen and the data for the contraction and carbon dioxide absorption calculated to butylene. The observed data follow:

Results of analysis of butylene residue.

	C. c.
Volume taken for analysis	2. 3
Volume of oxygen added	93. 81
Total volume for combustion	96. 11
Volume after combustion	90. 53
Contraction from combustion	5. 58
Volume after carbon dioxide absorption	82. 86
Carbon dioxide from combustion	7. 67

The equation for the reaction of butylene with oxygen is as follows:

$$C_4H_8+6O_2=4CO_2+4H_2O$$

According to this equation a contraction of 3 volumes and a carbon dioxide absorption of 4 volumes result when a given volume of butylene reacts with oxygen. The volumes for contraction and carbon dioxide obtained in the above analysis, 5.58 c. c. and 7.67 c. c., are almost in the ratio of 3:4, the discrepancy being within the allowable error in making the analysis; hence the data were calculated to butylene. The quantity of gas from which the butylene is computed was so small that there might easily have been a trace of butane present. However, this quantity as compared to the original volume was only 0.11 per cent, so that the butane content, if any, was practically insignificant. Benzene should have appeared in this last fraction, but as it did not satisfactorily it was determined from a separate quantity of gas.

The volume of gas from the various fractions, exclusive of the benzene, was 1782+167+21.1+2.3 c. c., or 1972.4 c. c. The pro-

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portion of benzene in the gas, as found by a separate analysis, is 1.33 per cent. Then 1.33 per cent of 2048 c. c. equals 27.2 c. c., so that the computed volume of constituents recovered is 1972.4 c. c. plus 27.2 c. c., or 1996.6 c. c., which is within 1.6 c. c. of the quantity (1995 c. c.) that was fractionated. Considering the number of times the different fractions of gas were handled and measured in the fractionation analysis, this result is not a bad check on the operation.

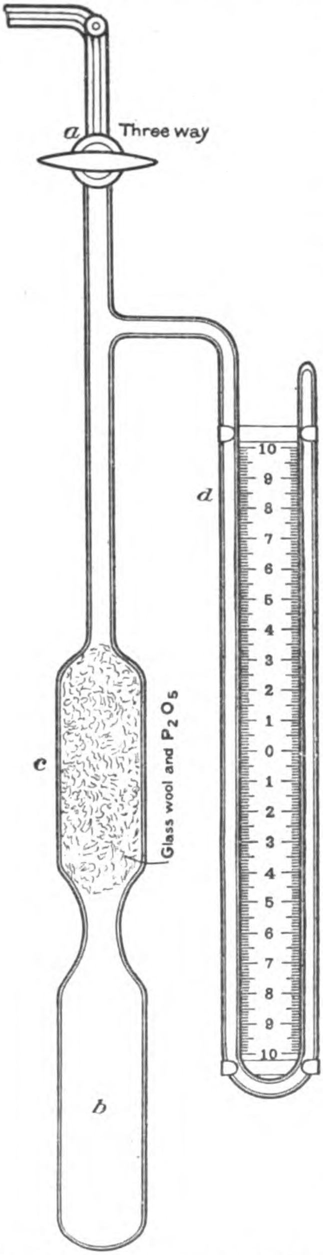

FIGURE 5.—Apparatus for the determination of benzene in artificial illuminating gas.

DETERMINATION OF BENZENE.

For the benzene determination a separate quantity of gas was used, as previously stated. In this analysis use was made of a method suggested by Dr. G. A. Hulett, consulting chemist of the Bureau of Mines, for the determination of water vapor in air. Hulett suggested that the sample of air, with its moisture, be cooled at the temperature of liquid carbon dioxide, the air removed with a mercury pump, and the water vapor determined, after removal of the cooling medium, by measuring its pressure. The principle was readily applied to the determination of benzene in illuminating gas.

The procedure adopted was as follows: The gas was freed of carbon dioxide and introduced into the liquefaction bulb *b* (fig. 5), cooled at a temperature of −78° C.,[a] and as much gas removed with the pump as possible. The phosphorus pentoxide in bulb *c* removed the water vapor. The stopcock *a* on the bulb was then closed and the Dewar flask containing the cooling medium removed. The condensed liquid in the bulb *b* was then vaporized and its pressure read on the manometer *d*. From this pressure and the original pressure of the gas was calculated the percentage of benzene in the gas. The results of two determinations are shown in the following table:

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[a] Readily obtained by mixing solid carbon dioxide with acetone.

Results of two determinations of benzene in illuminating gas.

Test.	Original pressure of gas (mm. of mercury).	Partial pressure of benzene vapor (mm. of mercury).	Illuminants found in distillate, percentage of original gas.	Calculation of benzene.	Benzene in gas.
					Per cent.
No. 1	744	10	7.32	$\frac{10\times100}{744}$	1.34
No. 2	744	9	7.39	$\frac{9\times100}{744}$	1.31

The total content of illuminants in the artificial illuminating gas of Pittsburgh was determined by the ordinary method of combustion and absorption in fuming sulphuric acid to be 8.67 per cent (p. 21). In making the benzene analyses the distillate from the benzene determinations was analyzed by absorbing the remaining illuminants in fuming sulphuric acid. There was removed from the distillates 7.32 and 7.39 per cent, respectively, of the original volumes of gas taken for the analyses. These percentages plus those of the benzene found, 1.31 and 1.34 per cent, equal 8.66 and 8.70 per cent, the average being almost identically the same as the quantity of total illuminants found in the gas by previous analysis.

Benzene reacts with oxygen as follows:

$$C_6H_6+7.5\ O_2=6CO_2+3HO$$

For a given quantity the contraction is 2.5 volumes and the carbon dioxide absorption is 6 volumes. The following data show the results of an analysis of the residual vapor that was held in the liquefaction bulb (fig. 1) when the gas was cooled at a temperature of $-78°$ C. Before analysis the benzene vapor was diluted with air.

Analysis of benzene vapor.

Item.	C. c.
Volume taken for analysis	28.29
Volume of oxygen added	51.94
Total volume for combustion	80.23
Volume after combustion	75.47
Contraction from combustion	4.76
Volume after carbon dioxide absorption	64.25
Carbon dioxide from combustion	11.42

The ratio between the carbon dioxide absorption and contraction is almost exactly 6:2.5, showing that the vapor contained in the determination was benzene. Traces of other easily condensible vapors may have been present but apparently these, if present, were in such small quantity as to be negligble. The vapor pressure of benzene at $-78°$ C. was not ascertained, but apparently it is very small. Benzene boils at 80° C. and 760 mm. pressure; at $-20°$ C. the tension is, according to Regnault, 5.76 mm.[a] The authors prepared saturated vapors of benzene by shaking pure benzene in a container with dry air. It was a simple matter to prepare unsaturated vapors by diluting the saturated vapors with air. The quantity of benzene vapor in the air was checked by combustion analysis.

A number of tests were made to determine the saturation limits of benzene in air for different temperatures by the method just described. It was found that at −78° C. all of the benzene could be separated from the air. Analyses of the distillates and residues were made to ascertain whether that at the temperature of −78° C. all of the benzene remained in the liquefaction bulb.

The foregoing method, therefore, seems to be well adapted for determination. A mercury pump, a liquefaction bulb, a gas burette for introducing the gases, and a Dewar flask for holding the refrigerant are required. A temperature of −78° C. can easily be obtained by mixing with acetone or alcohol the carbonic acid snow from commercial tanks. The gas does not have to be even measured; all that is necessary is to introduce the gas into the liquefaction bulb at atmospheric pressure and then read the barometer.

COMPLETE ANALYSIS OF PITTSBURGH ILLUMINATING GAS.

The results of the complete analysis of the artificial gas used in Pittsburgh, as found by these methods, were as follows:

Results of complete analysis of Pittsburgh gas.

Constituent.	Formula.	Per cent.	Constituent.	Formula.	Per cent.
Carbon dioxide	CO_2	2.63	Ethylene	C_2H_4	6.05
Oxygen	O_2	.81	Propylene	C_3H_6	.60
Carbon monoxide	CO	13.25	Butylene	C_4H_8	.11
Hydrogen	H_2	37.33	Benzene	C_6H_6	1.33
Methane	CH_4	31.13	Nitrogen	N_2	4.23
Ethane	C_2H_6	2.10			
Propane	C_3H_8	.43			100.00

INCOMPLETE ANALYSIS OF A DIFFERENT SAMPLE OF THE GAS.

The analysis of another sample of this gas, collected about seven weeks before the one already given, is presented here to show the marked uniformity of the gas. The benzene was not determined in this analysis, because at that time the method had not been perfected.

Results of analysis of earlier sample of Pittsburgh gas.

Constituent.	Formula.	Per cent.	Constituent.	Formula.	Per cent.
Carbon dioxide	CO_2	2.40	Ethane	C_2H_6	1.92
Oxygen	O_2	.61	Propane	C_3H_8	.32
Carbon monoxide	CO	13.63	Ethylene	C_2H_4	6.36
Hydrogen	H_2	37.13	Propylene	C_3H_6	.70
Methane	CH_4	30.92	Butylene	C_4H_8	.12

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[a] Landolt and Börnstein, Physikalish-chemische Tabellen, 1905, p. 143.

HEATING VALUE OF THE ILLUMINANTS IN THE GAS.

In calculating the heating value of artificial illuminating gas from an ordinary analysis the value assigned to the illuminants is usually only an approximation, because their constituents have not been exactly determined. By means of the method described in this publication, the exact composition of the illuminants can be determined. The heating value calculated from the complete analysis is given in the following table:

Heating value of illuminants in artificial gas of Pittsburgh.

Constituent.	B. t. u. per cubic foot (at 0° C. and 760 mm. pressure).[a]	Quantity in one cubic foot of gas.	Heating value.
		Cubic foot.	*B. t. u.*
Ethylene	1,673	0.0605	101.21
Propylene	2,509	.0060	15.05
Butylene	3,265	.0011	3.59
Benzene	4,012	.0133	53.36
Propane	2,654	.0035	9.29
		.0844	182.50

[a] Calculated from values found by Thomsen, which are given in large calories per gram-molecule in Landolt and Börnstein, Physikalish-Chemische Tabellen, 1905, p. 425.

According to the above calculations, the illuminants have a heating value, at 0° C. and 760 mm. pressure, of $\frac{182.50 \times 100}{8.44}$, or 2,162 B. t. u. per cubic foot. The authors have included propane in the illuminants ordinarily determined by absorption in fuming sulphuric acid because propane dissolves somewhat in the acid, just how much is not known. Methane and ethane are slightly soluble,[a] and unquestionably propane is much more so, because the higher paraffins are more soluble than the lower ones. If the propane be excluded the heating value of the illuminants becomes $\frac{173.2 \times 100}{8.09}$, or 2,141 B. t. u. per cubic foot, at 0° C. and 760 mm. pressure.

COMPOSITION OF THE ILLUMINANTS IN CARBURETTED WATER GAS AND COAL GAS.

In making the illuminating gas used in Pittsburgh 1 part of carburetted water gas is mixed with 3 parts of coal gas. The following experiments show the composition of the illuminants in the carburetted water gas and of those in the coal gas. The method of separating the illuminants was the same as that used in separating the illuminants in the mixed gas.

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[a] See Burrell, G. A., and Seibert, F. M., The sampling and examination of mine gases and natural gas Bull. 42, Bureau of Mines, 1913, p. 47.

COMPOSITION OF THE COAL GAS.

The composition of the illuminants in the coal gas before mixing with water gas is given in the table following. Column 1 shows the constituents in the gas as determined by the ordinary method and column 2 as determined by the fractionation analysis:

Composition of coal gas.

Constituent.	By ordinary analysis.	By fractionation.
	Per cent.	*Per cent.*
Carbon dioxide (CO_2)	1.4	1.4
Oxygen (O_2)	.5	.7
Carbon monoxide (CO)	8.0	7.9
Hydrogen (H_2)	50.3	50.6
Methane (CH_4)	30.9	31.1
Ethane (C_2H_6)	1.0	.9
Illuminants	3.9	
Ethylene (C_2H_4)		2.1
Propylene (C_3H_6)		.3
Butylene (C_4H_8)		.1
Butane (C_4H_{10})[a]		
Propane (C_3H_8)[a]		
Vapor having an inappreciable pressure at −78° C.		1.4
Nitrogen (N_2)[b]	4.0	3.5
	100.0	100.0

[a] Less than 0.1.
[b] Determined by difference.

In the analysis of the mixed coal and water gas, the vapor that had no appreciable pressure at a temperature of −78° C. was carefully examined, and was found to be benzene within the error of making the determination by combustion analysis. In the above analysis, this examination was not made, hence the notation is simply as given in the table. The 1.4 per cent of vapor represents that which had an inappreciable pressure at −78° C. Benzine undoubtedly predominates, probably to the exclusion of all except traces of other easily condensible vapors.

The total percentage of illuminants as determined by fractionation, 3.9 per cent, is the same as was obtained by absorption in fuming sulphuric acid.

COMPOSITION OF THE CARBURETTED WATER GAS.

The composition of the carburetted water gas is shown in the table following. Column 1 shows the constituents as determined by ordinary analysis, and column 2 as determined by fractionation.

Composition of the carburetted water gas.

Constituent.	By ordinary analysis.	By fractionation.
	Per cent.	*Per cent.*
Carbon dioxide (CO_2)	4.8	4.8
Oxygen (O_2)[a]		
Carbon monoxide (CO)	30.0	29.8
Hydrogen (H_2)	32.3	32.0
Methane (CH_4)	13.1	13.1
Ethane (C_2H_6)	3.0	2.9
Illuminants	15.9	
Propane (C_3H_8)		.3
Ethylene (C_2H_4)		9.8
Propylene (C_3H_6)		2.8
Butylene (C_4H_8)		1.7
Vapor having an inappreciable pressure at −78° C		1.5
Nitrogen (N_2)[b]	.9	1.3
	100.0	100.0

[a] Samples contained about 2.5 per cent of oxygen as received at the laboratory, due no doubt to faulty sampling; the results have been calculated to an air free basis.

[b] By difference.

The proportion of illuminants, as determined by absorption in fuming sulphuric acid, was 15.9 per cent, and as determined by fractionation was 16.1 per cent.

RELATIVE PROPORTIONS OF ILLUMINANTS IN THE COAL GAS, THE WATER GAS, AND THE MIXED GAS.

The proportions of the various hydrocarbons that constitute the illuminants in the artificial gas of Pittsburgh is as follows:

Proportions of hydrocarbons that constitute the illuminants.

Constituent.	Coal gas.	Carburetted water gas.	Mixed coal and carburetted water gas.
	Per cent.	*Per cent.*	*Per cent.*
Ethylene (C_2H_4)	53.8	60.9	71.5
Propylene (C_3H_6)	7.7	17.4	7.2
Butylene (C_4H_8)	2.6	10.6	1.2
Propane (C_3H_8)		1.8	4.6
Butane (C_4H_{10})			
Benzene (C_6H_6), or gases held at −78° C	35.9	9.3	15.5
	100.0	100.0	100.0

Ethylene and other olefine hydrocarbons are shown to be present in the largest proportion.

EXPERIMENTS WITH GAS SUPPLIED TO NEW YORK CITY.

Artificial gas used in New York City was also analyzed by the fractionation methods. In separating the gases a more rapid method of fractionating was used than in previous work.

In former experiments the authors refractionated a particular fraction until the gases obtained were analytically pure. The same procedure was followed in fractionating coal gas. At the temperature of liquid air, the first fraction consisted of methane, nitrogen, carbon monoxide, hydrogen, and oxygen with a little ethane and ethylene, and the residue contained some of the five gases first mentioned. Hence the distillate and residue were refractionated until the gases were free from ethane and ethylene and the residue contained none of the five gases.

PROCEDURE IN TESTS.

The procedure adopted in analyzing the New York City gas is faster and more economical in the use of liquid air. In the case of coal gas, for instance, first as much gas as possible is removed at the temperature of liquid air, yielding a fraction A. The residue is subjected to distillation at a temperature not higher than – 140° C., yielding a distillate B, then at a temperature not higher than – 120° C., resulting in a distillate C, next at a temperature not higher than – 78° C., forming a distillate D. The four fractions thus obtained, A, B, C, and D, each contain some gases that belong properly to other fractions and must be purified by further fractionating. As each distillate was obtained it was removed from the pump and transferred to another container, the residue being left in the liquefaction bulb. For instance, after the first distillate was removed (at the temperature of liquid air), the liquid air was removed and the bulb surrounded with light gasoline of a temperature not higher than – 140° C., and so on.

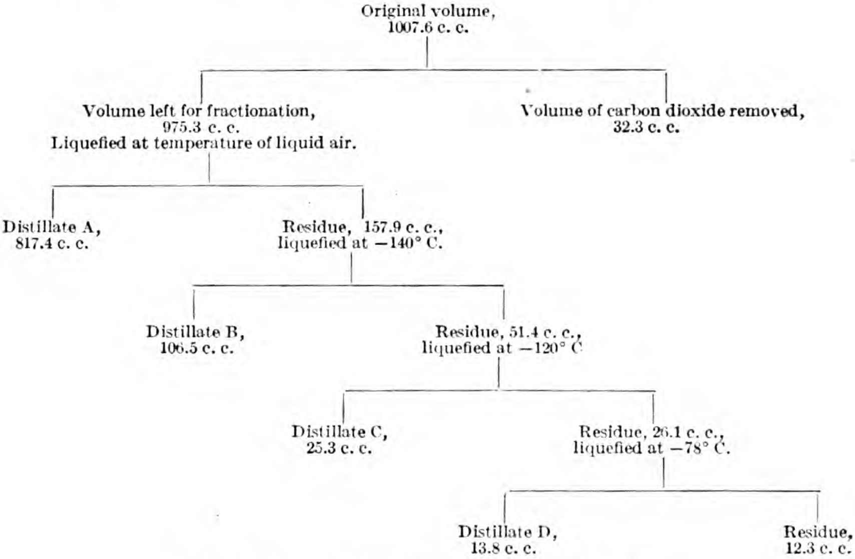

FIGURE 6.—Diagram showing results of first four distillations.

In fractionating the artificial illuminating gas of New York City the original volume of gas taken for analysis was 1,007.6 c. c., from which 32.3 c. c. of carbon dioxide was removed by caustic potash, leaving 975.3 c. c. for fractionation.

The method of obtaining the first four distillates A, B, C, and D, is clearly shown in figure 6. Distillate A was reliquefied at the temperature of liquid air and the distillate from it removed. The residue which was very small, was left in the liquefaction bulb and distillate B added to it. This mixture was then refractionated at a temperature not higher than −140° C. The distillate and residue so obtained were both refractionated again, because the pressure manometer showed that one fractionation was not enough. The residue from the last fractionation was left in the liquefaction bulb and the distillate C added to it, and so on. The last residue obtained at −78° C. was allowed to evaporate at room temperature and its pressure read. Previous experiments had shown that at −78° C. practically the only gas remaining in coal gas is benzene.

RESULTS OF ANALYSIS.

The results of the analysis were as follows:

Results of analysis of New York City illuminating gas.

Constituent.	Formula.	Per cent.	Constituent.	Formula.	Per cent.
Carbon dioxide	CO_2	4.7	Ethylene	C_2H_4	9.8
Oxygen	O_2	....	Propylene	C_3H_6	2.7
Carbon monoxide	CO	29.8	Butylene	C_4H_8	1.6
Hydrogen	H_2	32.0	Benzene	C_6H_6	1.5
Methane	CH_4	13.1	Nitrogen	N_2	1.7
Ethane	C_2H_6	2.8			
Propane	C_3H_8	.3			100.0

SEPARATION OF ETHANE AND ETHYLENE.

Some experiments were made in separating ethane and ethylene by fractional distillation in a vacuum at low temperatures. In the experiments previously cited the gases separated have widely different boiling points. Some of the constituents were obtained in pairs, for instance, ethane (boiling point −93° C.) and ethylene, (boiling point −103° C.) were not separated, neither were propane (boiling point −45° C.) and propylene (boiling point −51° C.). The mixture of ethane and ethylene was burned in oxygen, and from the carbon dioxide absorption and contraction produced, the percentage of each was calculated. The propane and propylene were determined in a similar manner.

In order to learn something of the limitations of the fractionation method of separating gases, for instance, the tediousness of separating ethane and ethylene (boiling points only 10° apart) in a mixture containing a large percentage of each, further experiments were made.

EXPERIMENTAL PREPARATION OF ETHANE.

Ethane was prepared by the electrolysis of a saturated solution of sodium acetate, the carbon dioxide evolved with the ethane being removed with caustic potash. Air or other gases trapped with the ethane were removed by fractional distillation in a vacuum at temperatures ranging from that of liquid air to −120° C.

PREPARATION OF ETHYLENE.

Ethylene was prepared by heating ethyl alcohol and sulphuric acid together at a temperature of 160° C. and was purified in the same way as the ethane. The purity of the two gases was determined by combustion analysis.

VAPOR PRESSURE OF ETHANE AND ETHYLENE.

It was first necessary to determine the temperatures at which the separation could be effected, that is, temperatures at which the partial pressures are such as to permit ethylene being removed, by enough fractionations, all of the ethane being finally left behind. At a temperature of −165° C. ethane has a vapor pressure of 1 mm. of mercury, and ethylene has at the same temperature a vapor pressure of 2 mm. At −170° the vapor pressure of ethylene was found to be 1 mm., whereas the manometer did not register any pressure for ethane. In determining these vapor pressures temperature readings were made with a pentane thermometer, which had been calibrated at four points. Pressures were registered with a mercury manometer provided with a scale graduated in millimeters.[a] The vapor pressures obtained showed that the separation could probably be accomplished at a temperature of −170° C. or slightly higher.

SEPARATION OF THE TWO GASES.

The two gases were mixed in equal proportions, 92 c. c. of ethane and 92 c. c. of ethylene. The fractionation was first tried at temperatures close to −170° C., but so much ethylene was present, its removal was so slow, and so much difficulty was experienced in maintaining a constant temperature for a long time, that higher temperatures and a wider range were employed in order to make an approximate separation. Hence, the first fractionations were made at temperatures of −160° to −155° C., the second at −165° to −155° C., the third at −168° to −165° C., and the last ones at −170° to −168° C. The various steps in the process are indicated in figure 7.

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[a] These vapor pressures, as well as those for propane, propylene, butane, butylene, acetylene, and carbon dioxide, will be published in another report of the Bureau of Mines.

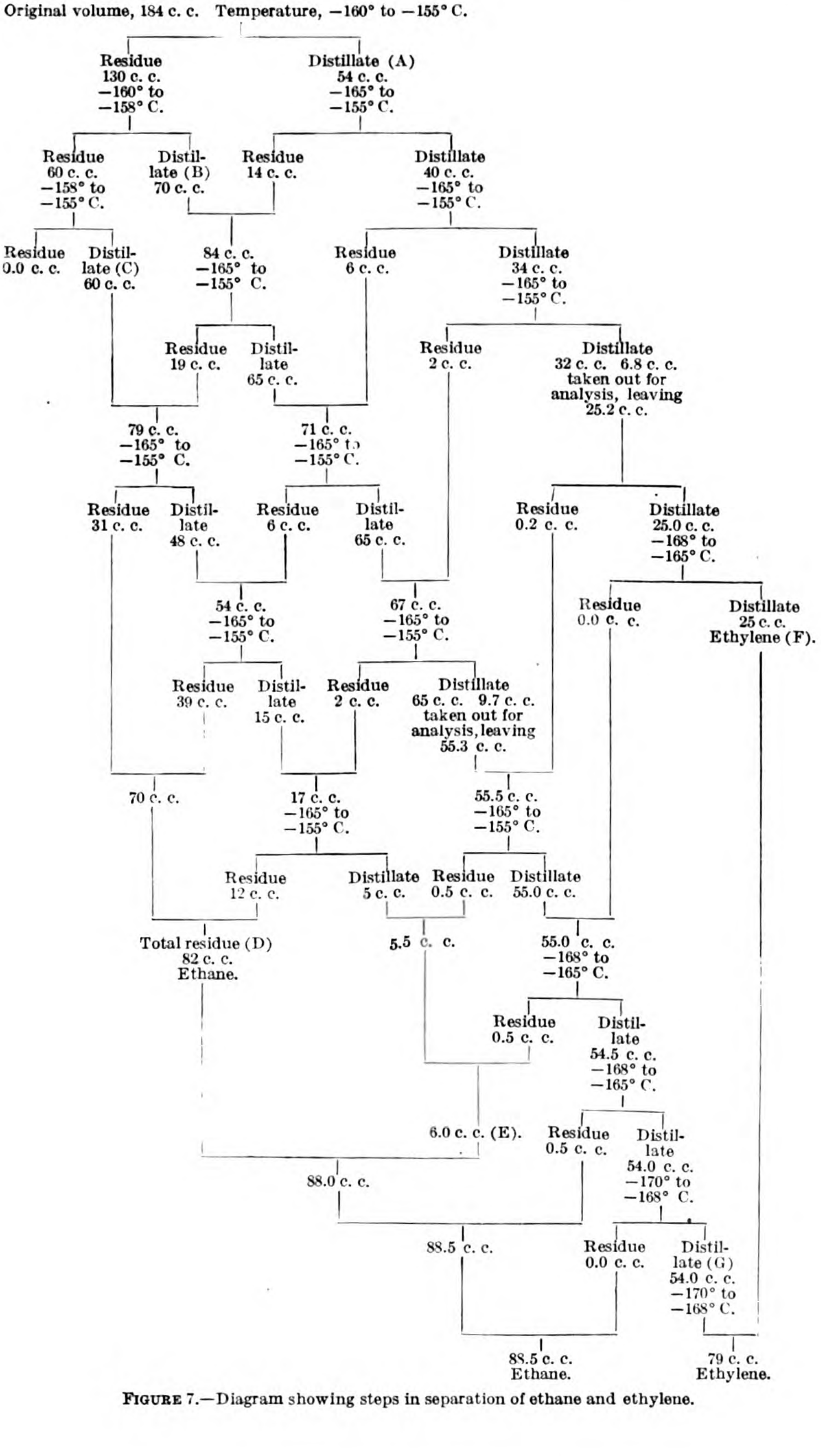
Original volume, 184 c. c. Temperature, −160° to −155° C.
Residue 130 c. c. −160° to −158° C.
Distillate (A) 54 c. c. −165° to −155° C.
Residue 60 c. c. −158° to −155° C.
Distil-late (B) 70 c. c.
Residue 14 c. c.
Distillate 40 c. c. −165° to −155° C.
Residue 0.0 c. c.
Distil-late (C) 60 c. c.
84 c. c. −165° to −155° C.
Residue 6 c. c.
Distillate 34 c. c. −165° to −155° C.
Residue 19 c. c.
Distil-late 65 c. c.
Residue 2 c. c.
Distillate 32 c. c. 6.8 c. c. taken out for analysis, leaving 25.2 c. c.
79 c. c. −165° to −155° C.
71 c. c. −165° to −155° C.
Residue 31 c. c.
Distil-late 48 c. c.
Residue 6 c. c.
Distil-late 65 c. c.
Residue 0.2 c. c.
Distillate 25.0 c. c. −168° to −165° C.
54 c. c. −165° to −155° C.
67 c. c. −165° to −155° C.
Residue 0.0 c. c.
Distillate 25 c. c. Ethylene (F).
Residue 39 c. c.
Distil-late 15 c. c.
Residue 2 c. c.
Distillate 65 c. c. 9.7 c. c. taken out for analysis, leaving 55.3 c. c.
70 c. c.
17 c. c. −165° to −155° C.
55.5 c. c. −165° to −155° C.
Residue 12 c. c.
Distillate 5 c. c.
Residue 0.5 c. c.
Distillate 55.0 c. c.
Total residue (D) 82 c. c. Ethane.
5.5 c. c.
55.0 c. c. −168° to −165° C.
Residue 0.5 c. c.
Distil-late 54.5 c. c. −168° to −165° C.
6.0 c. c. (E).
Residue 0.5 c. c.
Distil-late 54.0 c. c. −170° to −168° C.
88.0 c. c.
88.5 c. c.
Residue 0.0 c. c.
Distil-late (G) 54.0 c. c. −170° to −168° C.
88.5 c. c. Ethane.
79 c. c. Ethylene.

FIGURE 7.—Diagram showing steps in separation of ethane and ethylene.

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FIRST SERIES OF FRACTIONATIONS.

The 184 c. c. of ethane and ethylene was fractionated at temperatures of −160° to −155° C. The volume of distillate obtained was 54 c. c. This is designated as "Distillate A" in the diagram, figure 7. The residue from this distillation was refractionated at −160° to −158° C., yielding 70 c. c. of distillate B. The residue from this second distillation was refractionated at −158° to −155° C., and there was obtained 60 c. c. of distillate C. No residue was left.

At any of these temperatures all of the gas could be removed as a distillate in a comparatively short time by continuing the pumping. The object was simply to divide the original sample into several fractions, each containing considerably more of one constituent than the other so that an excessive amount of gas would not have to be removed at lower temperatures, where the distillation proceeds more slowly.

SECOND SERIES OF FRACTIONATIONS.

The first distillate (A) of 54 c. c. was refractionated at temperatures ranging from −165° to −155° C., yielding a distillate of 40 c. c. To the residue of 14 c. c. was added distillate B (70 c. c.), and this 84 c. c. was distilled at −165° to −155° C. It yielded 65 c. c. of distillate and 19 c. c. of residue. To this residue was added distillate C (60 c. c.), making 79 c. c., which was distilled at temperatures ranging from −165° to −155° C.; 45 c. c. of distillate and 31 c. c. of residue were obtained.

OTHER FRACTIONATIONS.

In all, 18 fractionations were made, and there was finally obtained 88.8 c. c. of ethane and 79 c. c. of ethylene. Two portions, one of 6.8 c. c. and one of 9.7 c. c. (total 16.5 c. c.) had been removed during the fractionation as shown in figure 7, in order to determine by combustion analysis the purity of the fractions. In each case the separation was found to be incomplete. If this portion, 16.5 c. c., be added to the final volume of ethane, 88.5 c. c., and the ethylene, 79 c. c., the result is 184.3 c. c., which is almost in agreement with the original volume taken, 184 c. c.

PURITY OF THE FRACTIONS.

Analyses of some of the fractions are given below to show their purity. The fractions were burned in oxygen and the percentage of each constituent calculated from the contraction and carbon dioxide absorption.

ANALYSIS OF THE ETHANE FRACTIONS.

Three analyses were made of the residue D (fig. 7). The total quantity of gas, ethane, collected at this point was 82 c. c. The data show the purity of the ethane.

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Results of three analyses of residue D, ethane.

Item.	Analysis 1.	Analysis 2.	Analysis 3.
	C. c.	*C. c.*	*C. c.*
Volume of gas taken for analysis	9.00	20.23	21.03
Volume of oxygen added	63.47	83.37	97.82
Total volume for combustion	72.47	103.60	118.85
Volume after combustion	49.84	53.22	66.57
Contraction from combustion	22.63	50.38	52.28
Volume after carbon dioxide absorption	31.77	12.81	24.45
Carbon dioxide from combustion	18.07	40.41	42.12
Ethane calculated from contraction	9.05	20.15	20.91
Ethane calculated from carbon dioxide absorption	9.04	20.20	21.06

According to the reaction, $C_2H_6 + 3.5O_2 = 2CO_2 + 3H_2O$, there result two volumes of CO_2 and a contraction of 2.5 volumes when a given volume of ethane reacts with oxygen. The results show that the observed data correspond well with the theoretical equation.

The results of an analysis of the distillate designated E in the diagram (6 c. c. of ethane) were as follows:

Results of analysis of distillate E, ethane.

Item.	C. c.
Volume of sample taken for analysis	6.00
Volume of oxygen added	75.43
Total volume for combustion	81.43
Volume after combustion	66.43
Contraction from combustion	15.00
Volume after carbon dioxide absorption	547.1
Carbon dioxide from combustion	11.72
Ethane calculated from carbon dioxide absorption	5.88
Ethane calculated from contraction	6.00

ANALYSES OF THE ETHYLENE FRACTIONS.

The following two analyses were made of the ethylene distillate (25 c. c.) denoted F in the diagram:

Results of two analyses of distillate F, ethylene.

Item.	Analysis 1.	Analysis 2.
	C. c.	*C. c.*
Volume of sample taken for analysis	9.00	9.20
Volume of oxygen added	47.10	43.76
Total volume for combustion	56.10	52.96
Volume after combustion	38.45	34.87
Contraction from combustion	17.65	18.09
Volume after carbon dioxide absorption	20.70	16.70
Carbon dioxide from combustion	17.75	18.17
Ethylene calculated from contraction	8.83	9.05
Ethylene calculated from carbon dioxide absorption	8.87	9.08

According to the reaction $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$, there result 2 volumes of carbon dioxide and a contraction of 2 volumes when a given quantity of ethylene reacts with oxygen. The results for the carbon dioxide absorption and the contraction, in the foregoing analyses, correspond with this reaction. The ethylene was not 100 per cent pure, however, probably because of a trace of air, although unfortunately this point was not determined.

The results of an analysis of the distillate G, 54 c. c., were as follows:

Results of analysis of distillate G, ethylene.

Item.	C. c.
Volume sample taken for analysis	19.55
Volume of oxygen added	73.18
Total volume for combustion	92.73
Volume after combustion	53.81
Contraction from combustion	38.92
Volume after carbon dioxide absorption	14.82
Carbon dioxide from combustion	38.99
Ethylene calculated from contraction	19.46
Ethylene calculated from carbon dioxide absorption	19.50

CONCLUSIONS.

Although in this experiment the separation of ethane and ethylene was complete within the error of making the analyses, the work involved is too tedious to be entirely satisfactory when each gas is present in considerable quantity. The ease with which gases having widely different boiling points are separated is in sharp contrast with the difficulty of separating ethane and ethylene.

SUMMARY.

This paper describes a method of separating natural gas into its paraffin hydrocarbons. Methane can be removed at the temperature of liquid air and the ethane separated from the propane, butane, etc., at temperatures ranging from −150° to −140° C. The propane is separated from the higher paraffins at temperatures ranging from −135° to −120° C. The method, although somewhat involved, is the only known method applicable to the separation of some hydrocarbons.

A method of separating the illuminants in coal gas is also described. The methane, hydrogen, carbon monoxide, nitrogen, and oxygen are first removed at the temperature of liquid air, the ethane and ethylene are removed at a temperature not higher than −140° C., the propane and propylene are removed at a temperature not higher than −120°, leaving the butylene, butane, and benzene as a residue. The benzene can be separated from the butane and butylene at a temperature of −78° C.

Benzene can be simply and quickly determined in coal gas or other mixtures by removing the carbon dioxide and water vapor, cooling the mixture at a temperature of −78° C., withdrawing the other gases at this temperature, and finally, after the refrigerant has been removed and the benzene vaporized, reading the vapor pressure on a mercury manometer.

Ethane and ethylene, whose normal boiling points are only about 10° C. apart, can not be satisfactorily separated by liquefaction and fractionation because of the tediousness of the operation.

By liquefaction and fractionation gases may be prepared in a condition of exceptional purity.

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